

**Physical, Chemical and Radiative Properties of Aerosols
in Sydney, Australia**

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Abstract

Atmospheric aerosols are one of the most spatially variable components of the Earth's atmosphere, and so require monitoring at a wide range of sites across the globe. We have been monitoring aerosol properties in Sydney for five years, studying both spectral optical thickness, and aerosol chemistry. From this data we have been able to extract typical (seasonal average) size distributions and refractive indices. Seasonal variability was found to be weak. We have constructed a model of Sydney aerosols, consistent with our observations, consisting of a mixture of continental aerosol and soot. Using this model we have computed the direct forcing, and the lower tropospheric flux divergence produced by Sydney aerosols. Due to the high soot content, we find that the forcing is actually reduced, while the flux divergence is significantly enhanced, when compared to 'clean' aerosol.

Introduction

Atmospheric aerosols are one of the most variable components of the Earth's atmospheric environment, and are known to influence the local energy budget in a number of ways. Of these, we may note especially direct forcing, where aerosols scatter solar radiation back to space, and energy absorption in the lower troposphere, which may have impacts on atmospheric vertical stability. Due to their inherent spatial and temporal variability, it is considered essential to monitor aerosol physical, chemical and optical properties at as many locations as possible, in order to build up a comprehensive picture of aerosols and their potential environmental impacts.

For the past five years we have been monitoring aerosol properties in Sydney, Australia, using ground-based radiometry, light scattering and chemical analysis. From this data we have been able to observe (weak) seasonal cycles in aerosol properties. We have taken these seasonally averaged data and computed both the radiative forcing, and flux divergence, of Sydney aerosols. Due to the relatively high elemental carbon content of these aerosols, the forcing is significantly reduced from what it would otherwise be. That is to say, Sydney aerosols reflect less sunlight than clean aerosols, and absorb more.

In section 2 we discuss the aerosol optical thickness data we have obtained, and examine the seasonal variability, which is seen to be weak. In section 3 we discuss the various sources of chemical and other data which we have used to determine both the refractive index, and single scattering albedo of these aerosols. By modelling Sydney aerosol as a mixture of continental aerosol and soot, we have generated the necessary input data to run our radiative transfer code to determine the radiative effects of this aerosol. These results are presented in section 4.

Optical Thickness Measurements

We have monitored the aerosol spectral optical thickness on a daily basis using a multifilter rotating shadowband radiometer (MFRSR) (Harrison et al. 1994) which is located on the Kensington campus of the University of New South Wales, in Sydney's eastern suburbs, at $33^{\circ} 55' 11.6''$ S and $151^{\circ} 13' 40.7''$ E, and 85m above sea level. This instrument has operated, with a few interruptions, from December 12 1995. It has one broad band, and 6 narrow bands (see Table 1), of which five are used to extract aerosol optical thickness data. On all suitable days, a Langley analysis was performed on both the morning and afternoon data, to obtain the atmospheric optical depth at each of these wavelengths. (The water vapour channel was analyzed separately – these results has been presented elsewhere: Taha and Box 2002.) A complete analysis of the time series of this data is being prepared for publication. The 615 nm channel is quite sensitive to ozone, while both the 502 and 673 nm channels are slightly contaminated. We have been able to separate the aerosol and ozone contributions very successfully using our recently developed covariance matrix technique (Taha and Box 1999).

In Figure 1 we present the morning and afternoon values of the aerosol optical thickness at 502 nm for the period September 1996 to September 1997, which shows that there was some seasonal variation, especially in the morning data. Day to day variability was, however, much larger. We have inverted a total of 237 data sets, using both the constrained linear inversion technique (King et al. 1978) and analytic eigenfunction theory (Box et al. 1992). Bimodal size distributions, with mode radii of 0.1 – 0.35 μm , and 0.6 – 0.85 μm , accounted for 82% of the inversions. The remaining 18% were either unimodal or simple power law distributions.

We broke the optical thickness data at each channel into the four seasons, to see what seasonal cycles could be detected: these seasonal values are presented in Table 2. These data show that such cycles are relatively weak (day-to-day variability was, as seen in Figure 1, much larger), with a minimum in spring. These eight average data sets were each inverted to obtain the corresponding aerosol size distribution. One example of the resulting distributions is shown in Figure 2.

Aerosol Chemistry Data

Aerosol samples have been collected by the Australian Nuclear Science and Technology Organization (ANSTO) since 1991, as part of their Aerosol Sampling Program (ASP). Samples have been routinely collected at a number of sites around the greater Sydney area every Wednesday and Sunday at these sites, using a PM_{2.5} sampler. These samples have then been subjected to ion beam analysis (IBA) using a 3MV van de Graaff accelerator, and analyzed using particle induced X-ray emission (PIXE), particle induced gamma ray emission (PIGME), and proton elastic scattering analysis (PESA) techniques. Between them, these techniques are sensitive to H, Li, B, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Ni, Zn, Br, and Pb with good sensitivity. Using assumptions as to chemical composition (Malm et al. 1994), plus principal component analysis, aerosol chemistry is then broken into six species: sulphate, soil, organic carbon, salt, smoke and black carbon. (The black carbon content is actually determined using the laser integrating plate method (LIPM).) Finally the reconstructed fine mass is compared with the gravimetric mass on the original filter. (Note that IBA is a non-destructive testing method, so that samples may later be analyzed by other techniques, such as ion chromatography, if desired.)

We have had access to this data from the Mascot sampling site, about 5 km from UNSW, which we assume to be reasonably representative of the aerosols in the air column above our radiometer (or at least of those in the atmospheric boundary layer). For 1997, the average fine particle mass concentration at Mascot was close to $10 \mu\text{g m}^{-3}$. Inorganic species comprised 30% of total mass ($\pm 15\%$), organic species were 23.4% ($\pm 15.4\%$), elemental carbon was 27.6% ($\pm 12.9\%$), windblown soil was 5% ($\pm 2.1\%$) and trace elements (such as Pb, Br, Zn and Mn) were 1.3% ($\pm 0.7\%$). (The ‘missing’ material was assumed to be water and nitrates.)

This data was used as input to the SCAPE2 thermodynamic model (Kim et al. 1993a; 1993b) in order to predict the details of the aerosol chemistry, and hence obtain key optical parameters. This model is capable of handling mixtures of ammonium, chloride, nitrate, sodium, sulphate and water, in equilibrium at the prevailing relative humidity. That is, the aerosol particles were assumed to be an internal mixture of these species. While this is clearly not true of all the particles in the aerosol, it should provide reasonable estimates of refractive index, humidity growth factor, and density.

The mean aerosol refractive index was then assumed to be derived from the volume-weighted molar refractivity. Similarly, the mean aerosol density was obtained from the volume-weighted component densities. It was found that, on average, the real part of the refractive index of Sydney aerosols could be expressed by the relation

$$n = 1.78(1 - RH)^{0.07} \quad (1)$$

where RH is the relative humidity (expressed as a fraction, not a per centage). This result is applicable for humidities up to around 95%. Similarly, the density is given by

$$\rho = 2.03(1 - RH)^{0.15} \quad (2)$$

A similar expression was fitted to the aerosol growth factor, namely

$$f(RH) \equiv m/m_{\text{dry}} = 0.84 (1 - RH)^{-0.26} \quad (3)$$

Determining the imaginary part of the aerosol refractive index is a much greater challenge. On a total of 6 days, we applied the diffuse-to-direct method (King and Herman 1979) in order to extract both the imaginary index, and the surface reflectivity. Although we were not able to retrieve the surface contribution consistently, results for the aerosol's index were reasonably consistent at 0.037 ± 0.0135 , with a corresponding single scattering albedo of 0.736 ± 0.028 . These values are also consistent with the relatively high elemental carbon content in the aerosol.

Radiative Impacts

Using the seasonal size distributions, and the inferred information on refractive index, we have computed the radiative forcing of Sydney aerosols using our version of the Fu and Liou radiative transfer code (Kay and Box 2000; Kay et al. 2000). This code uses the delta-four-stream method to perform multiple scattering calculations (Liou et al. 1988), and the correlated k-distribution method to perform spectral integrations (Fu and Liou 1992).

This code requires a detailed description of the optical characteristics of the atmosphere and underlying surface as inputs. We used temperature and humidity profiles which were reasonably representative of Sydney for each season, and assumed a vegetation surface, which may not be ideal, but is probably not too far from reality. For all calculations we assumed a solar zenith angle of 60° .

Finally we needed the aerosol optical properties over a very broad wavelength range: from 0.3 to 40.0 microns. To obtain this, we chose to model Sydney aerosols as an external mixture of continental aerosol and soot. We took the aerosol size distribution for each season, plus the spectral refractive index data for the mineral aerosol from the OPAC data base (Hess et al. 1998, d'Almeda et al. 1991), and computed the total optical thickness, scattering optical thickness, and asymmetry factor at a large series of wavelengths. These data were then band averaged over each of the six solar bands, and the twelve longwave bands. To this data, we added an amount of soot in order to achieve the appropriate values of optical thickness and single scattering albedo in the visible band. These values were allowed to vary somewhat to reflect the variability present in our original data.

We then ran our radiative transfer code for all eight cases, both with and without aerosols. We were interested in two quantities in particular, for both shortwave and longwave radiation. The first of these is the forcing, which is defined as the difference in net flux at the top of the atmosphere with and without aerosols. The second is the flux divergence in the lowest three kilometres, again with versus without aerosols.

The results for the shortwave regime are presented in Table 3. In all cases the forcing was negative, indicating that the aerosols were having a cooling influence on the energy budget. The magnitude of this forcing is around 1 Watt per square metre, in line with predicted values for anthropogenic aerosol forcing. However, for two of our data sets the forcing is a good deal smaller, in line with the smaller single scattering albedo values. This result is consistent with our earlier modelling results (Kay and Box 2000), and shows how critical this parameter can be.

The results for flux divergence also varied with single scattering albedo, as would be expected. In fact, we plotted flux divergence against the aerosol absorption optical thickness, and obtained an excellent straight line fit:

$$\Delta F = 800 \tau_{aer} (1 - \omega_0) \quad (4)$$

We also extracted the longwave values of both these quantities, and as expected they were both quite small: less than 0.25 Wm^{-2} for the forcing, and less than 1.0 Wm^{-2} , for the flux divergence.

Sydney aerosols differ from background aerosols mainly in their carbon content. Since radiative forcing is normally defined as the difference between the top-of-atmosphere flux with and without some change in atmospheric composition, we repeated our radiative transfer calculations, but this time assuming Sydney aerosol was entirely mineral. These results are also shown in Table 3, as the second entry for each season. When we compare these two sets of results, we see that the effect of the addition of elemental carbon to Sydney aerosols is to reduce the forcing by between 2.5 and 4 Wm^{-2} , which implies a (local) climate warming. We also see that, as expected, the carbon content leads to an increase in flux divergence of $8 - 10 \text{ Wm}^{-2}$. Thus, more solar energy is absorbed in the lower atmosphere, and less is both reflected to space, and absorbed at the ground. We also repeated the longwave calculations without the additional carbon, and found little difference. This is a result of the much smaller size of soot particles, compared to the mineral aerosol we have modelled with our retrieved size distributions. (Note that all our computations are for a cloud-free atmosphere, and should be reduced appropriately to allow for a realistic cloud fraction.)

Discussion

Sydney's aerosol levels are low by comparison with many large urban areas, and hence do not appear to exert a major climatic forcing. However, they do contain a significant elemental carbon content, which has the effect of absorbing, rather than scattering incoming solar radiation. The seasonality of Sydney aerosols is quite weak, with little variation in either aerosol loading or size distribution. (Day to day variability is much greater than seasonal.) Thus the results presented in Table 3 should be seen as a reflection of the variability in the radiative effects of Sydney aerosols.

Because of their high soot content, Sydney aerosols actually reflect less sunlight back to space, by between 2.5 and 4 Wm^{-2} . Thus, the urban/industrial pollution which Sydney actually contributes to the local atmospheric environment can be said to have a warming effect on the surrounding region. However, this warming is not felt at the surface, but rather in the lower troposphere, as the increase in flux divergence is considerably greater than the decrease in backscattering. In fact, the surface heat budget is actually reduced by around 5 Wm^{-2} .

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Table 1. MFRSR Spectral Band Locations, Bandwidths, and Main Trace Species.

Channel	Wavelength (nm)	Bandwidth (nm)	Trace species
1	broadband		
2	415.4	9.7	aerosol
3	501.7	10.1	aerosol and ozone
4	615.5	10.0	ozone and aerosol
5	672.7	10.0	aerosol and ozone
6	869.8	10.0	aerosol
7	933.6	11.2	water vapour

Table 2. Seasonal Mean and Standard Deviation of the Aerosol Optical Thickness

Season	Wavelength	AM: τ_{aer}	σ	PM: τ_{aer}	σ
DJF	416	0.0657	0.0522	0.0833	0.0529
	501	0.0610	0.0412	0.0696	0.0392
	616	0.0513	0.0313	0.0567	0.0285
	673	0.0479	0.0284	0.0534	0.0258
	870	0.0429	0.0243	0.0469	0.0234
MAM	416	0.0719	0.0425	0.0652	0.0518
	501	0.0618	0.0385	0.0571	0.0404
	616	0.0511	0.0289	0.0463	0.0287
	673	0.0472	0.0271	0.0422	0.0252
	870	0.0391	0.0259	0.0347	0.0203
JJA	415	0.0616	0.0411	0.0715	0.0379
	501	0.0589	0.0314	0.0626	0.0309
	616	0.0473	0.0234	0.0482	0.0236
	673	0.0423	0.0213	0.0429	0.0210
	870	0.0325	0.0208	0.0335	0.0157
SON	415	0.0471	0.0465	0.0760	0.0765
	501	0.0461	0.0375	0.0599	0.0444
	616	0.0372	0.0289	0.0442	0.0274
	673	0.0331	0.0260	0.0391	0.0237
	870	0.0229	0.0205	0.0310	0.0192

Table 3. Seasonal Forcing and Flux Divergence

First line with soot included, second line without soot.

Season	τ_{aer}	ω_0	Forcing	Flux divergence
DJF, am	0.0654	0.7508	-1.22	12.88
		0.8777	-3.79	6.23
DJF, pm	0.0790	0.7063	-0.39	18.31
		0.8722	-4.43	7.93
MAM, am	0.0683	0.7511	-1.36	13.40
		0.9004	-4.59	5.17
MAM, pm	0.0625	0.7104	-0.44	14.36
		0.9088	-4.40	4.24
JJA, am	0.0586	0.7696	-1.11	10.87
		0.9198	-3.89	3.57
JJA, pm	0.0695	0.7583	-1.47	13.41
		0.9266	-5.35	3.66
SON, am	0.0483	0.7495	-0.92	9.57
		0.9296	-3.72	2.32
SON, pm	0.0715	0.7343	-1.11	15.02
		0.9217	-5.47	4.07

Figure Captions.

Figure 1. Temporal variation of aerosol optical thickness at 0.502 nm. (a) Morning. (b) Afternoon.

Figure 2. Retrieved size distribution for summer (DJF) afternoon.

Table 3. Average Monthly Particle Mass and Growth Factor Fitting Parameters.

Month	Mass ($\mu\text{g}/\text{m}^3$)	α	γ	R^2
Jan.	5.18	0.51	0.57	1.00
Feb.	5.16	0.71	0.45	0.99
Mar.	7.13	0.52	0.48	0.99
Apr.	12.16	0.90	0.26	0.98
May	8.83	0.90	0.21	0.98
June	13.34	0.90	0.15	0.96
July	11.92	0.89	0.18	0.97
Aug.	12.10	0.91	0.17	0.97
Sep.	9.29	0.90	0.24	0.98
Oct.	11.34	0.57	0.38	0.99
Nov.	10.01	0.85	0.34	0.99
Dec.	9.96	0.51	0.52	0.99
Year	9.70	0.84	0.26	0.98